Atomic layer deposition of Al_2O_3 on GaSb using *in situ* hydrogen plasma exposure

Laura B. Ruppalt,[a] Erin R. Cleveland, James G. Champlain, Sharka M. Prokes, J. Brad Boos, Doewon Park, and Brian R. Bennett
Electronics Science and Technology Division, Naval Research Laboratory, Washington, DC 20375, USA

(Received 18 October 2012; accepted 8 November 2012; published online 3 December 2012)

In this report, we study the effectiveness of hydrogen plasma surface treatments for improving the electrical properties of GaSb/Al_2O_3 interfaces. Prior to atomic layer deposition of an Al_2O_3 dielectric, p-GaSb surfaces were exposed to hydrogen plasmas *in situ*, with varying plasma powers, exposure times, and substrate temperatures. Good electrical interfaces, as indicated by capacitance-voltage measurements, were obtained using higher plasma powers, longer exposure times, and increasing substrate temperatures up to 250 °C. X-ray photoelectron spectroscopy reveals that the most effective treatments result in decreased SbO_x, decreased Sb, and increased GaO_x content at the interface. This *in situ* hydrogen plasma surface preparation improves the semiconductor/insulator electrical interface without the use of wet chemical pretreatments and is a promising approach for enhancing the performance of Sb-based devices. [http://dx.doi.org/10.1063/1.4768693]

Antimonide-based compound semiconductors are receiving increased attention as potential candidates for the replacement of silicon in advanced complementary metal-oxide-semiconductor (CMOS) technologies; their high electron and hole mobilities, as well as relatively narrow bandgaps, make them particularly well-suited for high-speed, low power applications.[1–4] While both n- and p-channel devices have been demonstrated,[3–9] antimonide-based MOS device development has been impeded by the lack of a compatible, high-quality gate insulator. In particular, one desires a gate dielectric that forms a low-defect interface with the semiconductor, enabling free movement of the Fermi-level at the semiconductor-oxide boundary and supporting high carrier mobility operation. Unfortunately, unlike the silicon-silicon dioxide pair, the native III-V oxides do not satisfy this requirement; they are typically complex in structure and composition, tending to form heavily-defected semiconductor/insulator interfaces that pin the Fermi-level within the channel and limit the device's ability to modulate charge.

Recently, atomic layer deposition (ALD) of dielectrics has emerged as a potential alternative to natively grown oxides; reports of ALD-deposited insulators on GaSb have demonstrated good Fermi-level movement,[10–12] with several switching device demonstrations.[7–9] As-grown GaSb surfaces are generally not suitable for direct ALD growth, as they possess thin native oxide layers that pin the Fermi-level at the insulator/semiconductor interface. As the thermal desorption temperatures of these oxides generally exceed 450 °C,[13] wet etches are often employed to achieve a nearly oxide-free surface prior to ALD. Aqueous oxide removal treatments reported in conjunction with ALD on GaSb include: HCl,[7–12,14] $(NH_4)_2S$,[14,15] NH_4OH,[11,15] and HF.[11] Of these, HCl-based approaches have been the most effective at removing the native oxide and unpinning the semiconductor Fermi-level in fabricated devices.[11]

In this letter, we report an alternative *in situ* hydrogen plasma pre-treatment process for GaSb surface preparation prior to ALD Al_2O_3 dielectric deposition. Previous reports have shown that exposure to atomic and molecular hydrogen species can be an effective way to remove GaSb oxides while preserving the underlying semiconductor surface stoichiometry and morphology;[13,16–18] plasma treatments have also been used to improve the interface quality of ALD dielectrics on InGaAs surfaces.[19] Our *in situ* procedure avoids wet chemical etches and is completed immediately prior to ALD dielectric deposition, decreasing the likelihood of contamination or incidental surface oxidation between processing steps. MOS capacitors fabricated on GaSb samples subjected to hydrogen-plasma pretreatments and subsequent Al_2O_3 deposition exhibit excellent charge modulation and decreased frequency dispersion of accumulation capacitance, indicating a reduction in undesired states at the dielectric/semiconductor boundary and an improvement in the electrical interface.

500 nm p-type GaSb device layers were epitaxially grown by MBE on unintentionally doped GaSb (100) substrates. Device layers were Be-doped, with an acceptor concentration of $N_A = 2 \times 10^{17}\,cm^{-3}$. As-grown samples were loaded into a Beneq ALD system with a base pressure of 1 mTorr and equipped with a remote RF plasma shower-head. Prior to dielectric deposition, samples were exposed to a hydrogen plasma at 1.5 Torr; the substrates were placed approximately 4 cm below the lower electrode grid and, therefore, were not in direct contact with the plasma. The RF plasma power, plasma exposure time, and substrate temperature during exposure were varied for each sample. Following the hydrogen treatment, Al_2O_3 films were deposited via a plasma-enhanced ALD process using trimethylaluminum (TMA) as the metal precursor and oxygen plasma for the oxidation half-cycle. For all samples, the substrate temperature during ALD growth was held at 150 °C, and 100 alternating cycles of TMA and oxygen plasma exposure were completed, resulting in a ~16 nm dielectric film as confirmed by ellipsometry. After

[a]Electronic mail: laura.ruppalt@nrl.navy.mil.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
03 DEC 2012		**00-00-2012 to 00-00-2012**

4. TITLE AND SUBTITLE	5a. CONTRACT NUMBER
Atomic layer deposition of Al2O3 on GaSb using in situ hydrogen plasma exposure	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S)	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) **Naval Research Laboratory,Electronics Science and Technology Division,Washington,DC,20375**	8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSOR/MONITOR'S ACRONYM(S)
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**5**	

dielectric deposition, samples were annealed in forming gas (9/1 N_2/H_2) at 350 °C for 30 min, conditions previously reported to improve dielectric properties of ALD Al_2O_3 films.[8] Circular MOS capacitors ranging in diameter from 60 μm to 100 μm were patterned on the insulator/semiconductor stacks by standard lithographic techniques. Ti/Au (100/1000 Å) gate metal deposition was accomplished via e-beam evaporation, oxide mesas were defined using an aqueous 10:1 buffered oxide etch, and top-side Ohmic substrate contacts were made by Pd/Pt/Au (120/100/1000 Å) e-beam evaporation. Capacitance-voltage (C-V) measurements were acquired at room temperature at frequencies ranging from 4 kHz to 2 MHz using a Keithley 4200 semiconductor characterization system. For all measurements, the substrate was grounded while the gate voltage was swept across the range of interest. A 50 mV_{rms} AC signal was superimposed onto the gate voltage to enable capacitance extraction. To evaluate changes in semiconductor surface composition due to plasma exposure, X-ray photoelectron spectroscopy (XPS) measurements were obtained on a second set of GaSb samples using a Thermo-Scientific K-alpha instrument. The GaSb samples for XPS were identical to those used for device fabrication, but without an Al_2O_3 top-layer. To prevent surface oxidation during the brief atmospheric transfer to the XPS system, the hydrogen-treated GaSb surfaces were passivated with 6 TMA micro-pulses (total TMA exposure <1 s) prior to removal from the ALD reactor.

C-V measurements acquired on samples subjected to treatments of varying plasma powers are plotted in Figures 1(b)–1(e), with results from a control sample without plasma treatment depicted in Figure 1(a). The as-grown GaSb substrates were exposed to 25 W, 50 W, 75 W, or 100 W hydrogen plasmas for 10 min prior to ALD dielectric deposition, with the substrate temperature during exposure held at 150 °C for all samples. The plotted capacitance has been normalized to the low-frequency accumulation capacitance. For the untreated sample, the capacitance is nearly static regardless of applied gate bias, indicating Fermi-level pinning at the insulator/semiconductor interface and suggesting a high density of interface states preventing adequate Fermi-level movement in the semiconductor. Additionally, there is significant frequency dispersion in accumulation, with the measured capacitance at negative voltage varying approximately 4.2% over the 4 kHz to 2 MHz frequency range. As the plasma power is increased to 25 W and 50 W, there is minimal change in the voltage-behavior of the C-V curves, though the frequency dispersion is reduced to 2.7% and 1.9%, respectively, pointing to a reduction in trap states energetically near the valence band. As the plasma power increases above 50 W, the density of undesired states at (or near) the interface decreases substantially, as indicated by the significant increase in capacitance swing achieved for high-frequency traces. By 100 W (Figure 1(e)), the C-V measurements take on the familiar frequency variation expected for MOS capacitors, indicating that the Fermi-level is sufficiently unpinned to sweep the semiconductor from accumulation through depletion to inversion. The ability of the MOS structures to modulate semiconductor charge can be quantified by the capacitance modulation, C_{mod}, calculated at the highest measurement frequency (2 MHz) by $C_{mod} = (C_{max} - C_{min})/C_{max}$, as depicted in Figure 1(f). Values of C_{mod} for

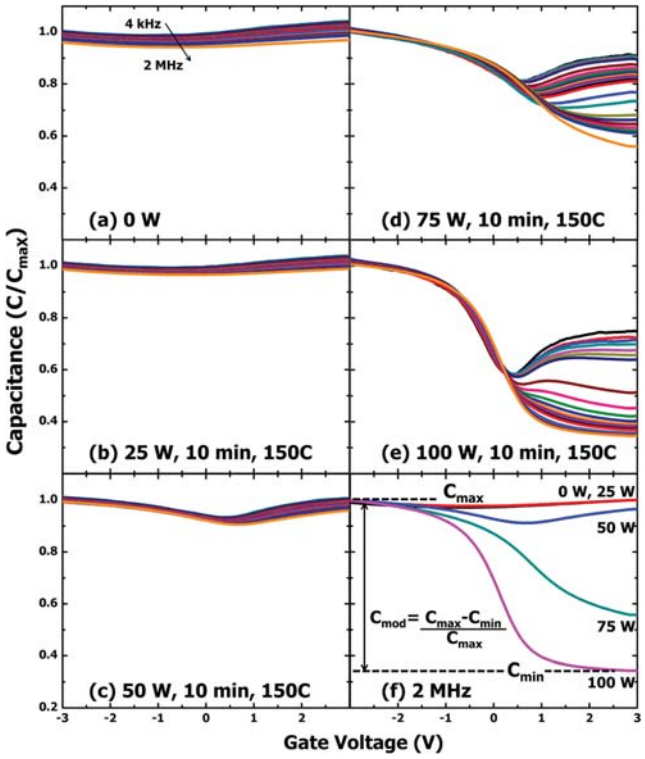

FIG. 1. Frequency-resolved C-V measurements for GaSb MOS capacitors exposed to 10 min, 150 °C plasma pretreatment with (a) 0 W (no plasma treatment), (b) 25 W, (c) 50 W, (d) 75 W, and (e) 100 W plasma power. (f) 2 MHz C-V curves from each sample in the power series showing variation in capacitance modulation. C_{mod} is calculated as indicated.

samples exposed to the varying power hydrogen plasmas are listed in Table I. Given the doping of the GaSb epilayer and the thickness of the Al_2O_3 dielectric film, the expected C_{mod} for a fully depleted device is estimated to be approximately 67%. The capacitance modulation for the hydrogen plasma exposed samples increases with increasing plasma power and, at 100 W, reaches a C_{mod} of 65.7%, close to the ideal value, indicating that it is possible to nearly fully deplete the semiconductor in the region of the dielectric interface.

The effect of increasing hydrogen plasma exposure time on the Al_2O_3/GaSb electrical interface is demonstrated in the

TABLE I. Hydrogen-plasma treatment summary.

	Power [W]	Time [min]	Temperature [°C]	C_{mod} (at 2 MHz) (%)
No Pretreatment	n/a	n/a	n/a	2.8
Power series	25	10	150	2.3
	50	10	150	8.8
	75	10	150	44.3
	100	10	150	65.7
Time series	50	1	150	4.4
	50	5	150	6.4
	50	20	150	65.3
	50	30	150	65.4
	50	60	150	65.0
Temperature series	50	10	200	52.1
	50	10	250	62.5
	50	10	300	3.2

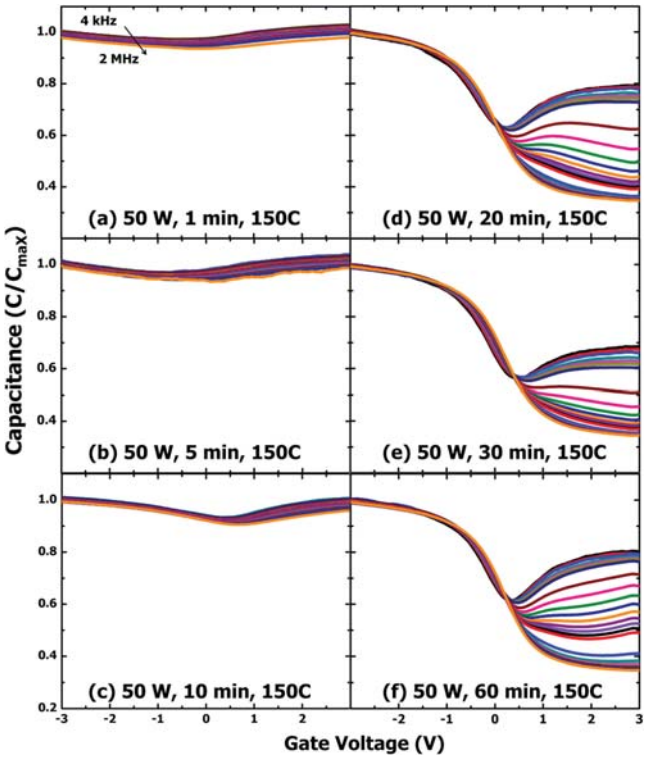

FIG. 2. Frequency-resolved C-V measurements for GaSb MOS capacitors exposed to 50 W, 150 °C hydrogen plasma pretreatment for (a) 1, (b) 5, (c) 10, (d) 20, (e) 30, and (f) 60 min.

C-V measurements of Figure 2. Substrates were exposed to 50 W hydrogen plasma treatments for 1, 5, 10, 20, 30, and 60 min, with the substrate temperature held at 150 °C during exposure for all samples. Measurements on the untreated sample (0 min) are shown in Figure 1(a) and C_{mod} values for all samples are listed in Table I. As the exposure time is increased from 0 min to 10 min, C_{mod} gradually increases from 2.8% to 8.8%, indicating a small improvement in electrical interface quality. At 20 min exposure time, C_{mod} increases to 65.3%, which is close to the ideal value of 67%, signaling a significant decrease in interface states. Further increasing the exposure time beyond 20 min provides minimal additional improvement in C_{mod} for the 50 W hydrogen plasma treatment.

C-V measurements on samples subjected to 50 W, 10 min hydrogen plasma exposures with varying substrate temperatures of 150 °C, 200 °C, 250 °C, and 300 °C are

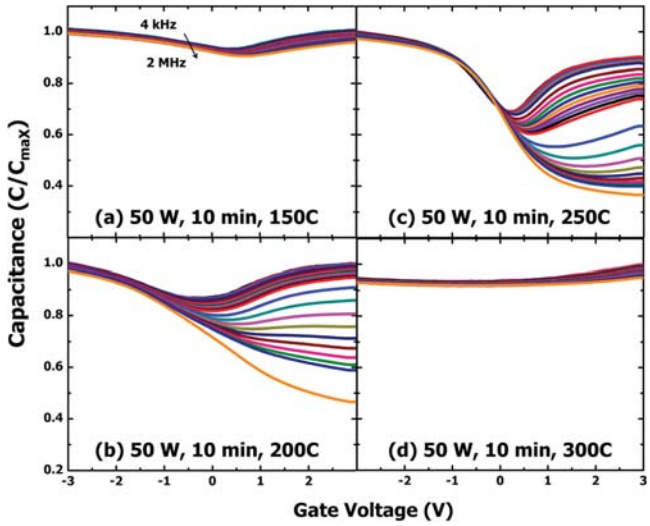

FIG. 3. Frequency-resolved C-V measurements for GaSb MOS capacitors exposed to 50 W, 10 min hydrogen plasma pretreatment with substrate temperature of (a) 150 °C, (b) 200 °C, (c) 250 °C, and (d) 300 °C.

shown in Figure 3; corresponding C_{mod} values are listed in Table I. Samples held at elevated temperatures for plasma treatment were cooled in the ALD chamber to 150 °C prior to oxide deposition. The plots of Figure 3 indicate that increasing substrate temperature above 150 °C improves the device performance, with the largest C_{mod} of 62.5% reached for the 250 °C sample. Further increasing the substrate temperature above 250 °C degrades the interface, with the measured capacitance nearly constant with applied gate bias and the semiconductor Fermi-level tightly pinned.

The composition of the hydrogen plasma exposed surfaces, prior to Al_2O_3 deposition, was investigated via XPS; scans of the Sb 3d and Ga 3d peaks for the 100 W power series sample (Figure 1(e)), as well as for the control sample with no plasma treatment (Figure 1(a)), are shown in Figure 4. For the 100 W sample, the twin SbO_x peaks at approximately 531 eV and 540 eV are reduced below the XPS detection level, indicating near complete removal of Sb-oxide from the semiconductor surface. Additionally, the Sb peaks at 528 eV and 537.5 eV are significantly lowered relative to the control. Given the minimal change in the Ga-Sb peak at ~19.2 eV between samples, we attribute the reduction in Sb signal to a decrease in elemental Sb at the surface. The GaO_x peak at 20.5 eV increases

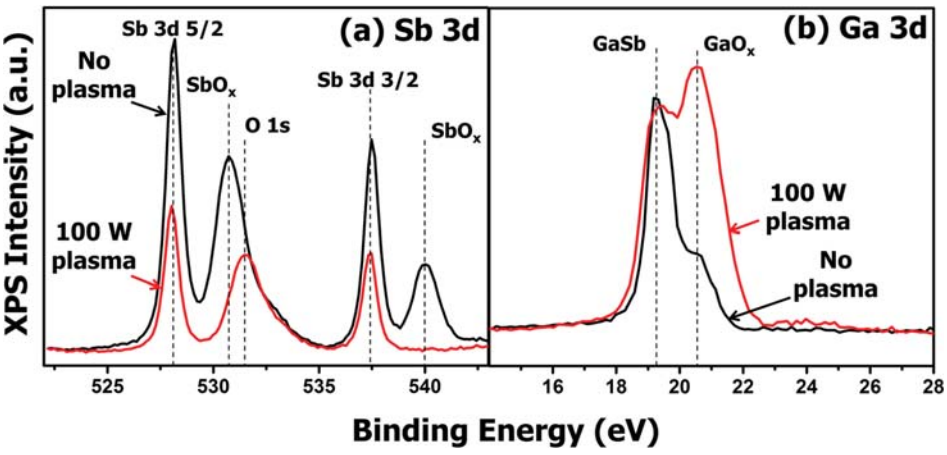

FIG. 4. (a) Sb 3d and (b) Ga 3d XPS scans from untreated (black) and 100 W, 10 min, 150 °C hydrogen-plasma treated (red) samples.

substantially on the hydrogen-exposed sample, signifying an increase in Ga-oxide content at the interface. Though not shown,[20] these trends are consistent for surfaces treated with varying plasma powers, exposure times, and substrate temperatures: samples exhibiting the greatest capacitance modulation ($C_{mod} > 60\%$) possess XPS spectra with no evidence of SbO_x, smaller Sb 3d peaks, and increased GaO_x 3d peaks, suggesting that good electrical performance may be correlated with the absence of Sb-oxide, a reduction in surface Sb, and the presence of Ga-oxide. The best performing samples exhibited the highest Ga-oxide content, implying that, rather than degrading electrical properties, interfacial Ga-oxide may serve to passivate defects at the semiconductor surface, as has been proposed for Al_2O_3/GaAs systems.[21]

These XPS results are consistent with previous reports,[13,17,18] which suggest that hydrogen species decompose Sb-oxide present in the native film, resulting in the formation of elemental Sb and Ga-oxides. Elemental Sb is then removed by thermal desorption or by formation of volatile SbH_3.[13] The generated Ga-oxide, is considerably more stable. Desorption of Ga-oxide has been reported at temperatures as low as 250 °C when in the presence of a hydrogen plasma in ultra-high vacuum.[17] However, XPS spectra obtained on our samples, for which hydrogen treatments were completed in low-vacuum, indicate the presence of Ga-oxide on the surface regardless of treatment power, time, or temperature.[20]

The C-V trends we observe for variations in plasma power, exposure time, and substrate temperature may be explained in the context of this proposed chemistry. Increasing the plasma power increases the density and kinetic energy of the atomic hydrogen species, enhancing removal of Sb-oxide and surface Sb. Increasing plasma exposure time increases the total dose of active hydrogen species interacting with the surface. Once the Sb-species are sufficiently removed and the Ga-oxide interlayer formed (which occurs at approximately 20 min treatment time for these samples), additional hydrogen exposure at the conditions used (50 W plasma power and 150 °C substrate temperature) appears to have minimal effect on the electrical interface. Increasing the substrate temperature up to 250 °C improves Sb desorption and may enhance Ga-oxide formation. AFM analysis indicates that further increasing the substrate temperature to 300 °C causes significant decomposition of the underlying GaSb substrate,[20] resulting in the degraded C-V characteristics observed in Figure 3(d).

The improvement in electrical interface achieved via *in situ* hydrogen plasma exposure has significant implications for Sb-based electronic devices. The Fermi level movement efficiency (FLME)

$$FLME = \frac{\left(\frac{dE_F}{dV_{gate}}\right)_{meas}}{\left(\frac{dE_F}{dV_{gate}}\right)_{ideal}} \times 100\% \quad (1)$$

is a measure of the structure's ability to control channel charge; a FLME of 100% indicates ideal charge-modulation. Figure 5 plots this quantity for the best performing sample from each series. FLME was determined using measured values calculated by Berglund's method[22] and ideal values calculated by an analytical solution to Poisson's equation. For all three samples, the efficiency exceeds 90% near the valence band edge and decreases as E_F moves deeper into the gap. For the 100 W and 30 min samples, FLME remains above 70% at midgap, indicating that good Fermi-level movement and charge modulation can be achieved for devices operating in the lower half of the bandgap. The FLME for the 250 °C sample drops below 50% at midgap, suggesting more limited Fermi-level movement in this sample, in line with its slightly lower measured C_{mod} value of 62.5%. Using the high-frequency/low-frequency method with quasi-static and 2 MHz CV measurements,[23,24] a mid-gap density of interface states of $\leq 1 \times 10^{13}\,cm^{-2}\,eV^{-1}$ was estimated for these samples.

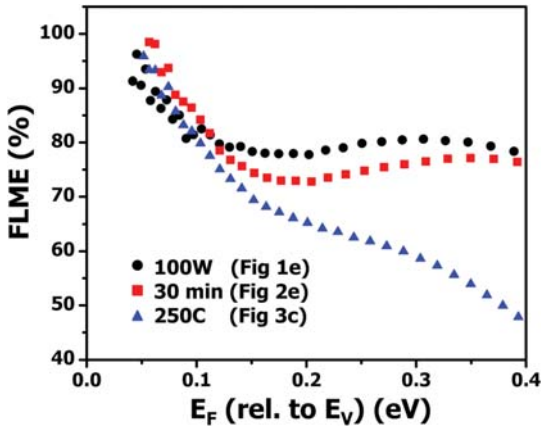

FIG. 5. Fermi-level movement efficiency for GaSb devices subjected to 100 W, 10 min, 150 °C (●), 50 W, 30 min, 150 °C (■), and 50 W, 10 min, 250 °C (▲) hydrogen plasma treatments.

In summary, we have evaluated the effectiveness of *in situ* hydrogen plasma treatments for improving the electrical properties of the GaSb/Al_2O_3 interface. C-V measurements indicate that good electrical interfaces can be achieved by subjecting the as-grown GaSb surface to hydrogen plasma prior to ALD Al_2O_3 dielectric deposition; the efficacy of the pretreatment can be tuned by varying the plasma power, plasma exposure time, and substrate temperature. All hydrogen plasma treatments resulted in a reduction in the frequency dispersion of accumulation capacitance compared to an untreated sample, indicating a decrease in interface states near the valence band. The best electrical characteristics, as assessed by total capacitance modulation, were obtained for higher plasma powers, longer exposure times, and increasing substrate temperatures up to 250 °C. Chemical analyses suggest that the improvement in electrical performance may be attributed to the elimination of Sb-oxide, the reduction of elemental Sb incorporation, and an increase in interfacial Ga-oxide. This *in situ* hydrogen plasma surface preparation technique eliminates the need for wet chemical etches and may also be applicable to the deposition of alternative high-k dielectrics such as HfO_2, making it a promising approach for realizing high performance Sb-based MOS-devices.

This work was supported by the Office of Naval Research. The authors thank Richard Magno, Theresa F. Chick, and Connie F. Kornegay for their contributions to device preparation and measurement.

[1]R. Chau, J. Brask, S. Datta, G. Dewey, M. Doczy, B. Doyle, J. Kavalieros, B. Jin, M. Metz, A. Majumdar, and M. Radosavljevic, in *2005 IEEE VLSI-TSA International Symposium on VLSI Technology*, *Hsinchu, Taiwan* (IEEE, 2005), pp. 13–16.
[2]R. Chau, S. Datta, M. Doczy, B. Doyle, J. Jin, J. Kavalieros, A. Majumdar, M. Metz, and M. Radosavljevic, IEEE Trans. Nanotechnol. **4**, 153 (2005).
[3]B. R. Bennett, R. Magno, J. B. Boos, W. Kruppa, and M. G. Ancona, Solid-State Electron. **49**, 1875 (2005).
[4]G. Dewey, M. K. Hudait, K. Lee, R. Pillarisetty, W. Rachmady, M. Radosavljevic, T. Rakshit, and R. Chau, IEEE Electron Device Lett. **29**, 1094 (2008).
[5]M. Radosavljevic, T. Ashley, A. Andreev, S. D. Coomber, G. Dewey, M. T. Emeny, M. Fearn, D. G. Hayes, K. P. Hilton, M. K. Hudait *et al.*, in *2008 IEEE International Electron Devices Meeting, San Francisco, California, USA* (IEEE, 2008), pp. 1–4.
[6]J. Nah, H. Fang, C. Wang, K. Takei, M. H. Lee, E. Plis, S. Krishna, and A. Javey, Nano Lett. **12**, 3592 (2012).
[7]A. Ali, H. Madan, A. Agrawal, I. Ramirez, R. Misra, J. B. Boos, B. R. Bennett, J. Lindemuth, and S. Datta, IEEE Electron Device Lett. **32**, 1689 (2011).
[8]A. Nainani, T. Irisawa, Z. Yuan, B. R. Bennett, J. B. Boos, Y. Nishi, and K. C. Saraswat, IEEE Trans. Electron Devices **58**, 3407 (2011).
[9]M. Xu, R. S. Wang, and P. D. Ye, IEEE Electron Device Lett. **32**, 883 (2011).
[10]A. Ali, H. S. Madan, A. P. Kirk, D. A. Zhao, D. A. Mourey, M. K. Hudait, R. M. Wallace, T. N. Jackson, B. R. Bennett, J. B. Boos, and S. Datta, Appl. Phys. Lett. **97**, 143502 (2010).
[11]A. Nainani, Y. Sun, T. Irisawa, Z. Yuan, M. Kobayashi, P. Pianetta, B. R. Bennett, J. B. Boos, and K. C. Saraswat, J. Appl. Phys. **109**, 114908 (2011).
[12]K. Suzuki, Y. Harada, F. Maeda, K. Onomitsu, T. Yamaguchi, and K. Muraki, Appl. Phys. Express **4**, 125702 (2011).
[13]E. Weiss, O. Klin, S. Grossman, S. Greenberg, P. C. Klipstein, R. Akhvlediani, R. Tessler, R. Edrei, and A. Hoffman, J. Vac. Sci. Technol. A **25**, 736 (2007).
[14]I. Geppert, M. Eizenberg, A. Ali, and S. Datta, Appl. Phys. Lett. **97**, 162109 (2010).
[15]S. McDonnell, D. M. Zhernokletov, A. P. Kirk, J. Kim, and R. M. Wallace, Appl. Surf. Sci. **257**, 8747 (2011).
[16]G. R. Bell, N. S. Kaijaks, R. J. Dixon, and C. F. McConville, Surf. Sci. **401**, 125 (1998).
[17]Z. Lu, Y. Jiang, W. I. Wang, M. C. Teich, and R. M. Osgood, J. Vac. Sci. Technol. B **10**, 1856 (1992).
[18]T. D. Veal, M. J. Lowe, and C. F. McConville, Surf. Sci. **499**, 251 (2002).
[19]A. D. Carter, W. J. Mitchell, B. J. Thibeault, J. J. M. Law, and M. J. W. Rodwell, Appl. Phys. Express **4**, 091102 (2011).
[20]E. R. Cleveland, L. B. Ruppalt, B. R. Bennett, and S. M. Prokes, "Effect of a H_2 Plasma on the Reduction of GaSb Native Oxide," Appl. Surf. Sci. (unpublished).
[21]C. W. Cheng, G. Apostolopoulos, and E. A. Fitzgerald, J. Appl. Phys. **109**, 023714 (2011).
[22]C. N. Berglund, IEEE Trans. Electron Devices **13**, 701 (1966).
[23]R. Castagne and A. Vapaille, Surf. Sci. **28**, 157 (1971).
[24]R. Engel-Herbert, Y. Hwang, and S. Stemmer, J. Appl. Phys. **108**, 124101 (2010).